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13. ABSTRACT (Maximum 200 Words)
Electrochromic polymers may prove especially important for a number of Air Force applications including chameleon coatings, informational displays, IR and microwave attenuation, and dialed tint windows. We have developed a new family of conjugated, redox active, polymers with controllable electronic band gaps that range from 1.1 eV to 4.0 eV, thus spanning from the NIR, through the entire visible spectrum, and into the UV. Studies of electrochromic polymers have been enhanced by the development of an electrochemical in-situ coloration efficiency method. Increasing the electron-rich character of the dioxyheterocycles, we have studied a new family of poly(3,4-alkylenedioxyppyroles) (PXDOPs). Electrochromism and ion transport studies of the PXDOPs show these polymers to switch at extremely low potentials and offer electrochromic properties not accessible with the PEDOT family of polymers. Donor-acceptor methodology has been used to prepare new materials which can be both p- and n-type doped with added benefit of being three color state electrochromics.

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Progress Report

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Controlled Redox and Electrical Properties in Polyheterocycles

Reporting Period:

December 1, 1999 to August 31, 2000

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November 14, 2000

1. Objectives

The effect of macromolecular structure and redox switching between charge states has been used to control the optoelectronic properties of conjugated polymers. Specific properties investigated include structure:property effects via model compounds, electrochromism, switchable electrical conductivity, and switchable IR and microwave absorption.

2. Status of Effort

Electrochromic polymers may prove especially important for a number of Air Force applications including chameleon coatings, informational displays, IR and microwave attenuation, and dialed tint windows. We have developed a new family of conjugated, redox active, polymers with controllable electronic band gaps that range from 1.1 eV to 4.0 eV, thus spanning from the NIR, through the entire visible spectrum, and into the UV. Studies of electrochromic polymers have been enhanced by the development of in-situ electrochemical coloration efficiency and conductivity methods. Increasing the electron-rich character of the dioxiheterocycles, we have studied a new family of poly(3,4-alkylenedioxyppyroles) (PXDOPs). Electrochromism and ion transport studies of the PXDOPs show these polymers to switch at extremely low potentials and offer electrochromic properties not accessible with the PEDOT family of polymers. Donor-acceptor methodology has been used to prepare new materials which can be both p- and n-type doped with added benefit of being three color state electrochromics.

3. Accomplishments

3.1 Electrochromic Polymers and Devices

Electrochromic Polymer Films. Electrochromism and ion transport through films of new poly(3,4-alkylenedioxyppyrole)s (PXDOPs), specifically poly(3,4-ethylenedioxyppyrole) (PEDOP), have been studied. After first characterizing the general electrochemistry (electropolymerization, polymer electrochemistry, spectroelectrochemistry, scan rate dependence, switching stability, etc.) of the family of XDOP's, the focus has now shifted to trying to map the electrochromism of PEDOT and PEDOP, specifically the coloration efficiency. Also important to this work is the study of differing counter-ions present in the supporting electrolyte solution.

Coloration efficiencies (CEs) are used as a measuring stick by which electrochromic (EC) materials of different types can be compared. CEs are measured by observing the injected/ejected charge as a function of unit area (Q_d) and the change in optical density ($\Delta OD(\lambda)$) as seen in Equation 1.

$$CE(\lambda) = \Delta OD(\lambda)/Q_d \quad (1)$$

where $\Delta OD(\lambda) = \log[T_b(\lambda)/T_e(\lambda)]$. The polymer, electrochemically deposited on an ITO-coated glass slide is placed in a monomer free electrolyte solution in a quartz cuvette equipped with a counter and reference electrode. The cell is placed in a UV-vis spectrometer and a varying

potential is applied, switching the polymer from the oxidized state to the neutral state (chronocoulometry). While the polymer is being switched, the $\Delta\%T$ at λ_{\max} monitored. The CE is then measured at 95% of $\Delta\%T$ since above that percentage it is impossible for the human eye to distinguish any further color change. Before any measurements are taken, the film is switched several times in order to "break in" the film.

Coloration Efficiency results were obtained for poly(3,4-ethylenedioxythiophene) (EDOT) using the results of Figure 1. The boxed switch is where the CE measurement was taken (see inset to Figure 1).

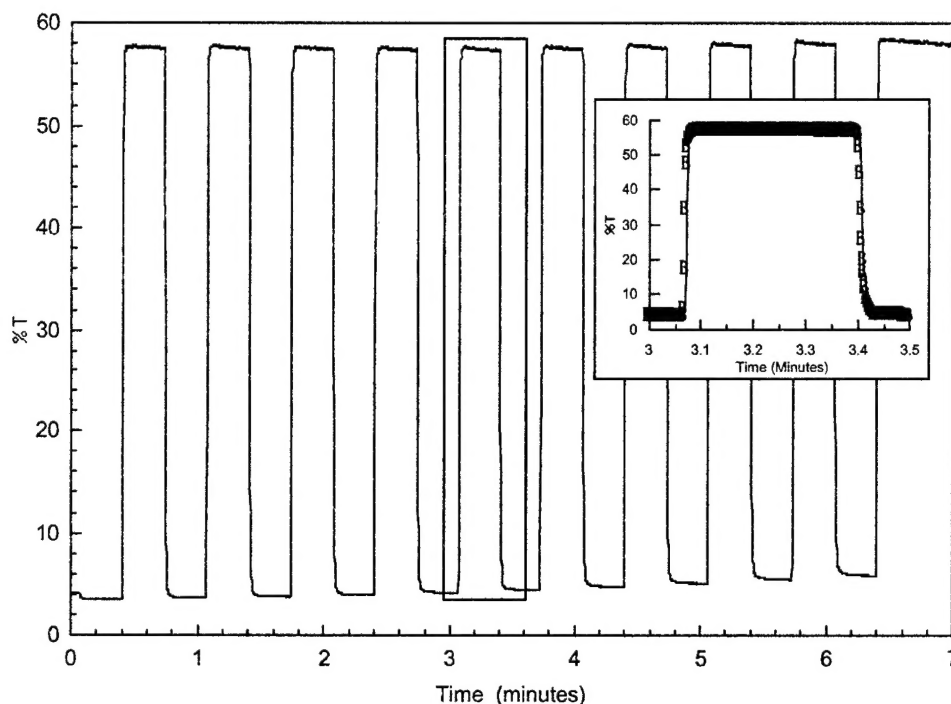


Figure 1 UV-vis switching experiment for PEDOT in 0.1 M TBAP/ACN. Inset: 5th switch that is boxed showing the number of points in one switch. This is also the switch where the values for the CE were taken.

The switches shown above were matched with the chronocoulometry experiment and the CE values were extracted. CE was measured versus the $\%\Delta\%T$ from 90 to 100% T and ranged from 300 to 900 cm^2/C with the highest CE observed at 90% of the full contrast of PEDOT. The values recorded for PEDOT are encouraging since CE values for a high-quality device have been measured as high as 1000 cm^2/C , even though it is difficult to compare these values with those for a film in solution.

Turning to the XDOP family, it was first necessary to determine optimum electropolymerization conditions. The repeated scanning electropolymerization of EDOP in 0.1 M TEAOTs/ACN yielded an unexpected result. There appears to be two polymer redox states during the polymerization (Figure 2). When a scan rate dependence experiment was attempted, the second peak at 0.6 V vs. Ag° dissipated after only 5 scans. This is markedly different when compared to the same electropolymerization in TBAPF₆/PC shown in Figure 3. Having these PXDOPs on hand now allows us to incorporate them into EC devices where their unique colorimetric properties complement the PXDOTs.

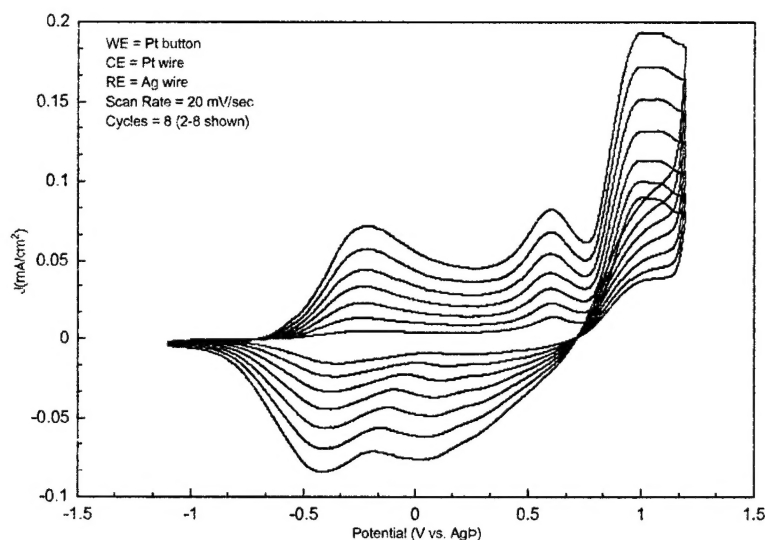


Figure 2 Electropolymerization of 0.01 M EDOP in 0.1 M TEAOTs/ACN.

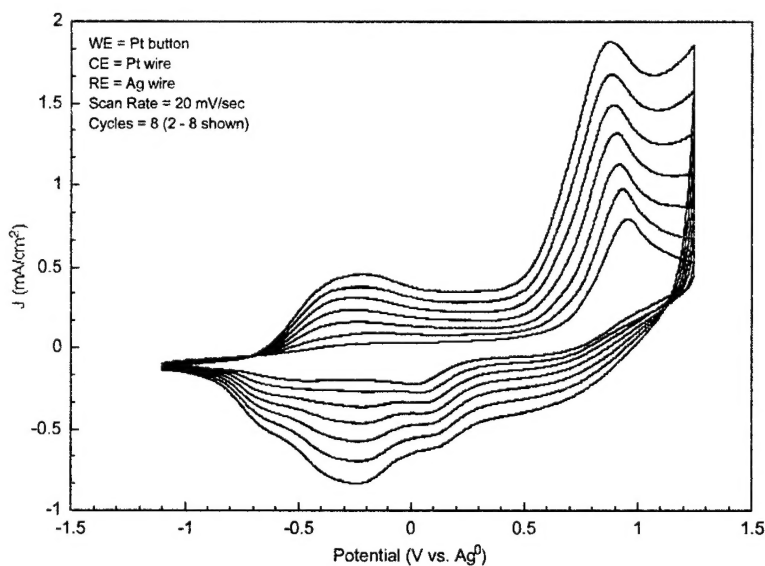


Figure 3 Electropolymerization of 0.01 M EDOP in 0.1 M TBAPF₆/PC.

High Contrast Multilayer Electrochromic Devices. The ability to tune color is an important goal in the design of electrochromic devices and the majority of the electrochromic polymers have a relatively narrow spectral color change. We have explored a strategy to broaden the absorption peak while at the same time to enhancing the contrast of an ECD by using laminate layers of cathodically coloring polymers with different λ_{max} . A diagram demonstrating the concept of complementary conducting polymers for use in laminate sandwich transmissive/absorptive ECDs is presented in Figure 4.

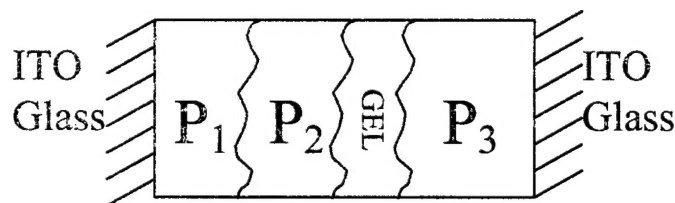


Figure 4. Schematic diagram of a tri-polymer laminate EC device

In this scheme, P_1 and P_2 are low band gap, cathodically coloring, conductive polymers. In one specific case, P_1 is PEDOP, that has a λ_{max} of 620 nm, and P_2 is PProDOT-Me₂ with its π to π^* transition at about 570 nm. The polymers are colored and opaque in the neutral state (PEDOP is red and PProDOT-Me₂ is blue-purple). Upon oxidation, lower energy transitions appear in the near infrared region and the π to π^* transitions lose their intensities, both materials becoming highly transmissive. For color and charge balance, a complementary high band gap polymer (P_3) is then selected. In its reduced form, the polymer is transmissive to a major portion of the visible spectrum and in its oxidized form the material becomes opaque.

Figures 5 and 6 show the visible spectrum of two laminate devices using two different high band gap polymers, PEDOT-NMeCz and PProDOP-N-PS, respectively. PEDOT-NMeCz is yellowish in the oxidized form, and consequently when the device is in its bleached state, the portion of the visible spectrum from 400 to 500 nm is less transmissive. Using PProDOP-NPrS as an anodically coloring polymer opens up the transmissivity window through the entire visible region and the device appears clear (%T=80% from 400 to 900 nm). The contrast of the second device reaches 55% at $\lambda_{\text{max}} = 580$ nm.

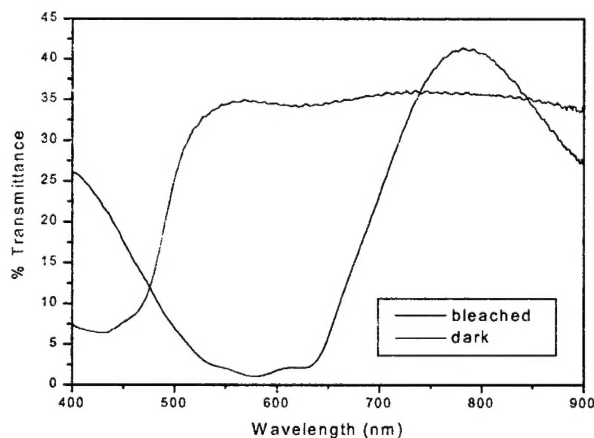


Figure 5. Transmittance of PEDOP/PProDOT-Me₂/electrolyte(LiClO₄ in PC)/PBEDOT-NMeCz device

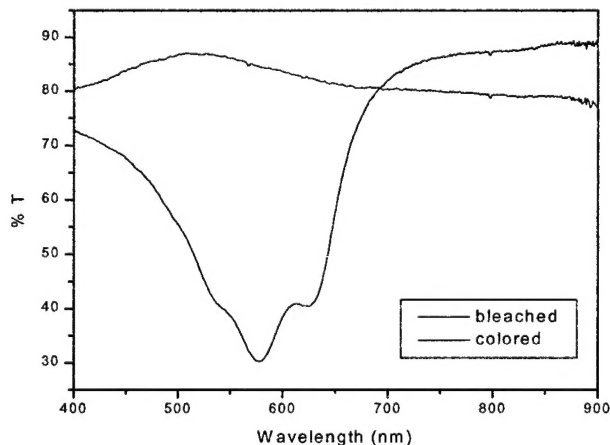


Figure 6. Transmittance of PEDOP/PProDOT-Me₂/electrolyte(LiClO₄ in PC)/PProDOP-N-PS device

These results are understood when one examines the spectroelectrochemistry of PProDOP-N-PS as shown in Figure 7. The neutral form of the polymer is transmissive through the entire NIR and visible regions of the spectrum, with an onset for the absorption at ca. 400 nm. With the π to π^* transition localized into the UV, the polymer is colorless to the eye.

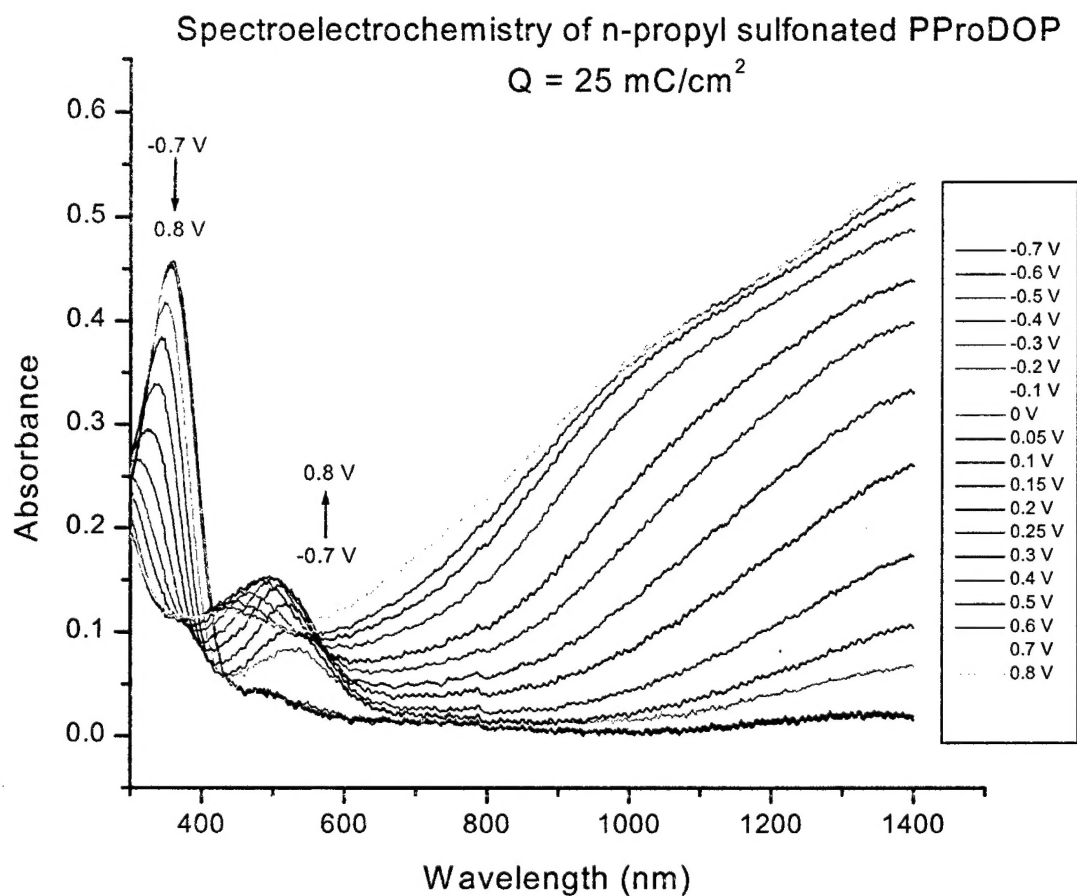


Figure 7. Spectroelectrochemical series for PProDOP-N-PS showing highly transmissive neutral state to the human eye.

3.2 Multi-Color Electrochromic Polymer Films. A series of alternating conjugated donor-acceptor polymers have been developed with reduced band gaps, n-type dopability and differently colored, conductive states. A unique property of this class of polymers is the existence of three distinct redox states (neutral, p-doped, and n-doped) yielding three different color states.

The cyanovinylene family of polymers obtained from the monomers shown in Figure 8 has been our model system for understanding how substitution affects band energies and electrochemical properties. The cyanovinylene family represents a class of molecules where the electron acceptor moiety is in direct conjugation with the polymer backbone.

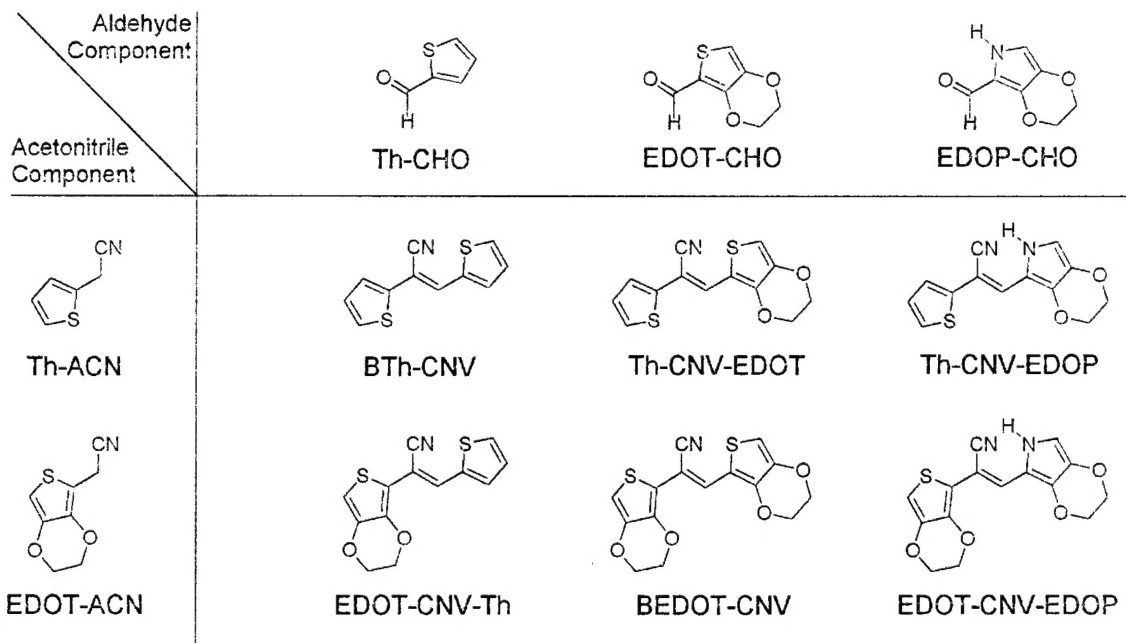


Figure 8. Cyanovinylene monomers available through Knoevenagel condensation.

In-Situ conductivity studies, a capability recently added to our repertoire for polymer characterization, indicates that the n-type conductivity for PBEDOT-CNV is between three and four orders of magnitude smaller than the p-type conductivity. Figure 9 details the electrochemical properties of PBEDOT-CNV and conductivity values obtained for this polymer. We have investigated the electrochemical properties of recently characterized conducting polymers by Differential Pulse Voltammetry (DPV) as a means of more accurately estimating electrochemical bandgaps and $E_{1/2}$ information for polymers. PBEDOT-CNV undergoes n-type doping at -1.27 V vs SCE.

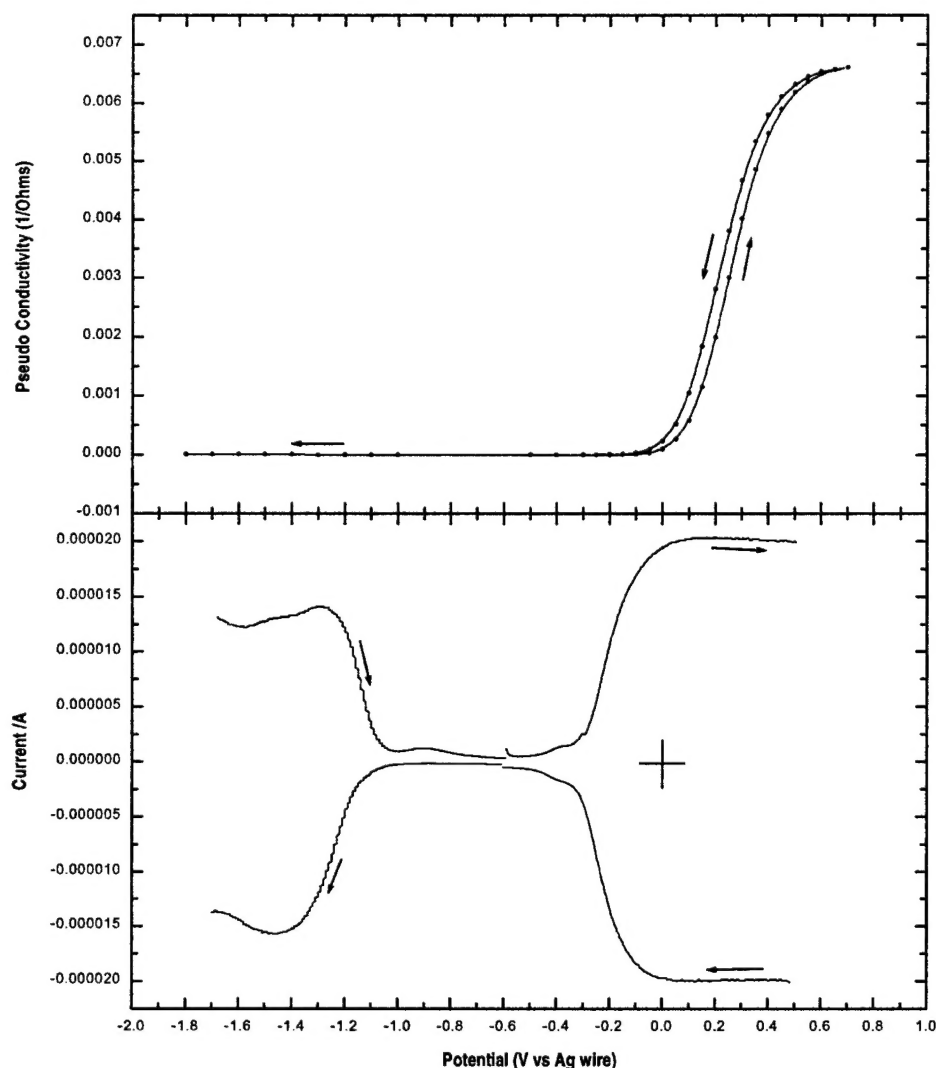


Figure 9. *In Situ* Conductivity of PBEDOT-CNV on a 10 μm gap IME (top) and DPV on 0.02 cm^2 Pt button electrode (bottom). Characterization in ACN/TBAP in a dry box.

As an alternative to the cyanovinylene family of materials where conjugation proceeds through the acceptor unit, we are continuing to develop the dicyanomethylidene fluorenone family of materials as well. This class of polymers has properties that are influenced by the inductive effect of the electron withdrawing group which is not in direct conjugation with the polymer backbone. The crystal structure for BEDOT-DCF, one of two monomers in this group, is shown in Figure 10. The monomer is mostly planar with a slight bowing of the fluorenone core and a twist to one of the EDOT moieties in the backbone. The TMS groups are included for enhanced solubility during monomer and polymer synthesis and are removed during electropolymerization. This family of polymers reduces at potentials (-0.7 V vs SCE) that are quite anodic in comparison to other polymers of this type.

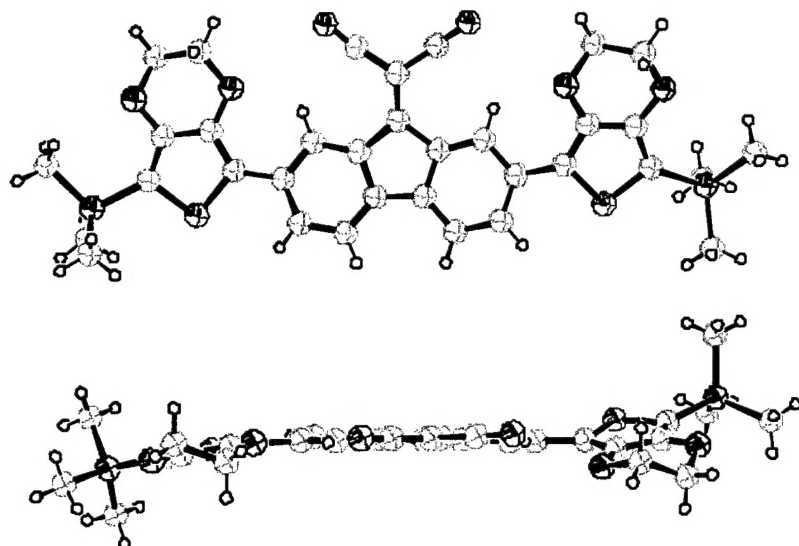


Figure 10. X-ray crystal structure of BEDOT-DCF showing both top view and side view explaining planarity.

A third donor-acceptor system we have investigated includes the pyridopyrazine (PyrPyr) family and includes both the bis-thienyl and bis-EDOT derivatives shown in Figure 11.

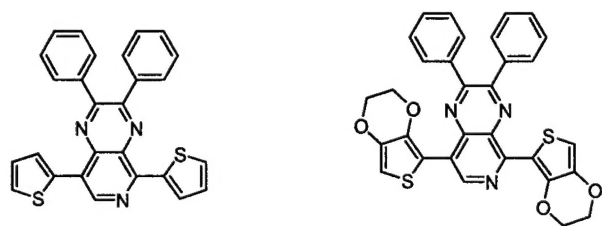


Figure 11. BTh-PyrPyr and BEDOT-PyrPyr

Figure 12 displays the electrochemical behavior of PBEDOT-PyrPyr indicating both a p-type and n-type doping process. The neutral form of the polymer is bright green. The oxidized form is a dirty green-gray color. Attempts to discern the reduced form's (n-doped) color failed due to delamination of the film from the electrode's surface. The synthesis of the bis-TMS derivative has been completed and its polymerization should lead to better film adhesion. The p-type doping of this polymer is very similar to the characteristics of PBEDOT-Pyr. However, the onset of n-type doping has shifted almost 1 V anodic due to the stronger acceptor ability of the PyrPyr unit. PBEDOT-PyrPyr has a band gap of 1.2 eV with a λ_{max} of 750 nm as determined by spectroelectrochemistry. This is in the extreme red region of the visible spectrum. PBTh-PyrPyr has a band gap of 1.6 eV.

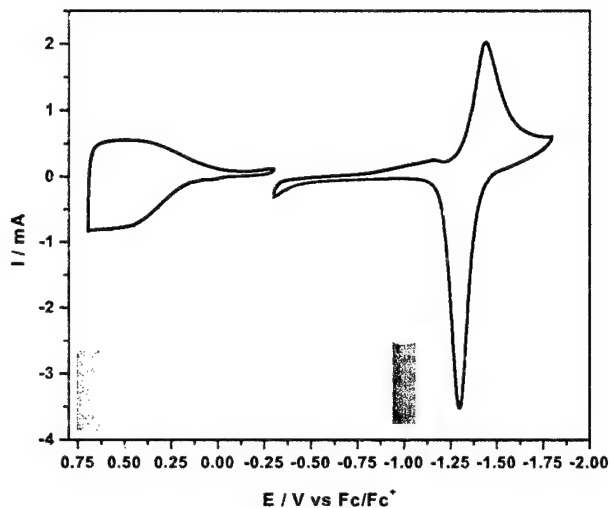


Figure 12 p-Type and n-type doping of PBEDOT-PyrPyr

Figure 13 describes the relative energies of the HOMO and LUMO of PBTh-Pyr, PBEDOT-Pyr, PBTh-PyrPyr, and PBEDOT-PyrPyr. EDOT's affect on the HOMO is evident in its higher energy when compared to thiophene. The affect of the PyrPyr unit can also be seen in the lower energy of its LUMO when compared to Pyr. Unlike the claims of others, the use of D-A copolymers does result in band gap compression.

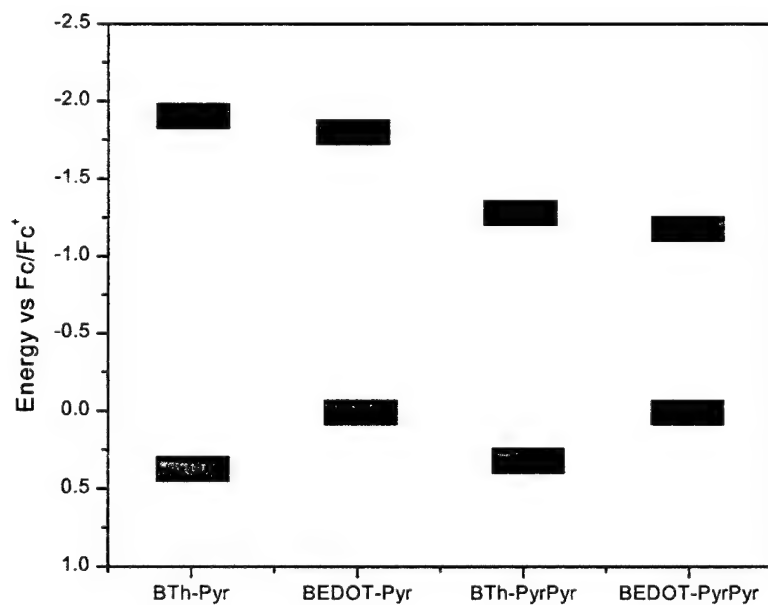


Figure 13. HOMO-LUMO plot for the bis-thienyl/EDOT pyridine based family of polymers

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Peer Reviewed Publications

1. Thomas, C. A., Zong, K., Schottland, P., Reynolds, J. R.
Adv. Mater., **12**, 222-225 (2000).
"Poly(3,4-alkylenedioxyppyroles) as Aqueous Compatible Conducting Polymers for Biomedical Applications"
2. Gaupp, C. L., Zong, K., Schottland, P., Thompson, B. L., Reynolds, J. R.
Macromolecules, **33**, 1132-1133 (2000).
"Poly(3,4-ethylenedioxyppyrole): Organic Electrochemistry of a Highly Stable Electrochromic Polymer"
3. Wang, F., Wilson, M. S., Rauh, R. D., Schottland, P., Thompson, B. C., Reynolds, J. R.
Macromolecules, **33**, 2083-2091 (2000).
"Electrochromic Linear and Star Branched Poly(3,4-Ethylenedioxythiophene-Didodecyloxybenzene) Polymers"
4. Thompson, B. C., Schottland, P., Zong, K., Reynolds, J. R.
Chem. Mater., **12**, 1563-1571 (2000).
"In-Situ Colorimetric Analysis of Electrochromic Polymers and Devices"
5. Harrison, B. S., Ramey, M. B., Reynolds, J. R., Schanze, K. S.
J. Am. Chem. Soc., **122**, 8561-8562 (2000).
"Catalytic Fluorescence Quenching of a Poly(*p*-phenylene)-Based Cationic Polyelectrolyte"

6. Schottland, P., Zong, K., Gaupp, C. L., Thompson, B. C., Thomas, C. A., Giurgiu, F., Hickman, R. H., Abboud, K., Reynolds, J. R.
Macromolecules, **33**, 7051-7061 (2000).
"Poly(3,4-alkylenedioxy pyrrole)s: Highly Stable Electronically Conducting and Electrochromic Polymers"
7. Groenendaal, L. B., Jonas, F., Freitag, D., Pielartzik, H., Reynolds, J. R.
Adv. Mater., **12**, 481-494 (2000).
"Poly(3,4-Ethylenedioxythiophene) and Its Derivatives: Past, Present and Future"

AFOSR Related Publications In Press and Submitted

1. Reynolds, J. R., Epstein, A. J.
Adv. Mater., in press.
"ICSM 2000: Over Twenty-Five Years of Synthetic Metals"
2. Somez, G., Schottland, P., Zong, K., Reynolds, J. R.
J. Mater. Chem., submitted for publication
"Highly Transmissive and Conductive Poly(3,4-alkylenedioxy pyrrole) (PXDOP) Films Prepared by Air or Transition Metal Catalyzed Chemical Oxidation"
3. Zong, K., Reynolds, J. R.
J. Org. Chem., submitted for publication.
"3,4-Alkylenedioxy pyrroles: Functionalized Derivatives as Monomers for New Electron-Rich Conducting and Electroactive Polymers"

TRANSITIONS

1. a) Reynolds/Florida, b) multi-color carbazole based electrochromic polymers which switch between yellow, green and blue colored states, c) Dr. Bert Groenendaal, AG Bayer, Krefeld, Germany (32 3 444 3224), d) Bayer researchers have investigated the electrochromic properties of some of our functionalized BEDOT-Cz based polymers for EC displays which may prove useful in camouflage and other commercial applications (signs/large area displays).
2. a) Reynolds/Florida, b) conducting hyperbranched and dendrimer polymers, c) Drs. David Rauh and Fei Wang, EIC Laboratories (781-769-9450), d) "Processible Conductive Resin for High Temperature Applications", F33615-97-C-5090. The UF group supplies synthetic and electrochemical expertise to EIC. A full spectroscopic and colorimetric analysis of conducting star polymers prepared at EIC was accomplished. These star polymers are potentially useful in EC displays which may prove useful in camouflage and other commercial applications (signs/large area displays).
3. a) Reynolds/Florida, b) redox switchable conducting polymers for microwave devices, c) Dr. John Stenger-Smith, Naval Air Warfare Center, China Lake, CA (760-939-1661), d) Electrochromic polymers developed in AF funded program demonstrate excellent microwave switching properties for electromagnetic shutters with application to radar and antenna type devices.
4. a) Reynolds/Florida, b) redox switchable conducting polymers for modulating infrared reflectivity from metals, c) Dr. Henry Everitt and Dr. Jack Rowe at ARO (919-549-4369), DARPA/HIDE Program and ARO/IR MURI, d) Electrochromic polymers developed in AF funded program demonstrate excellent contrast and switching properties in reflective devices for controlling IR reflectivity off of a metallic surface. Application to controlled emissivity surfaces and camouflage.
5. a) Reynolds/Florida, b) conductive cladding materials using redox doped conducting polymers with controlled electrical and optical properties, c) Dr. Hilary Lackritz, Gemfire, Inc. (650-849-6800), d) advanced displays. A set of PANI and PEDOT blends in amorphous and crystalline hosts has been investigated as potential electrode materials. These can be applied as cladding layers on non-linear optical polymers in advanced displays.
6. a) Reynolds/Florida, b) transport studies of conducting polymer free-standing films, c) Prof. Art Epstein, Ohio State (614-292-1133), d) Metallic conductors. Using multiple methods of DC transport, AC transport, EPR, and microwave studies the electronic properties of a series of poly(3,4-alkylenedioxythiophenes) have shown that some polymers have electrical properties on the metallic side of the insulator:metal transition. In order for polymers to ultimately be used as current carrying components in wires and electronic circuits (printed) metallic conductivity will be required.

7. a) Reynolds/Florida, b) water soluble PEDOTs for electrostatic adsorption processing c) Dr. Jeff Baur, AFRL/MLBP (937-255-9146), d) Polymers for photovoltaic devices. Successful development of polymer-based PV devices require donor and acceptor polymers with controlled band states. Electron rich water soluble PEDOTs have been supplied for ESA processing and use as electron donor components in photovoltaic devices.

Awards and Honors received by the PI (life-time received):

University of Florida, Research Foundation Fellowship 1999